Vehicle Technologies Office

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BAT343: Silicon and Intermetallic Anode Portfolio Strategy Overview

June 20, 2018

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Overview

- Vehicle Technologies Office Energy Storage Overview
- Cost Scenarios for Different Chemistries
- VTO Roadmap
- Silicon Anode Key Results
- Silicon Anode Focus Areas
- SEISta Overview
- Si Deep Dive Overview
- Questions?
- Panel Discussion

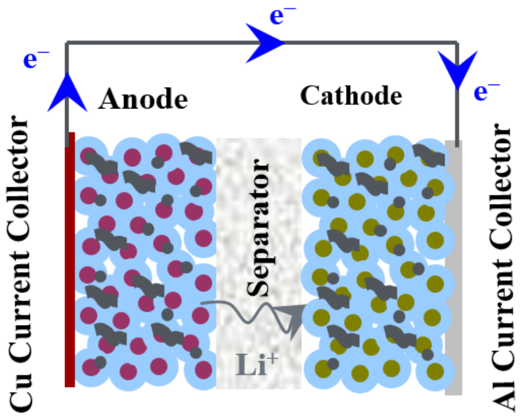
VTO Energy Storage R&D Overview and Strategy

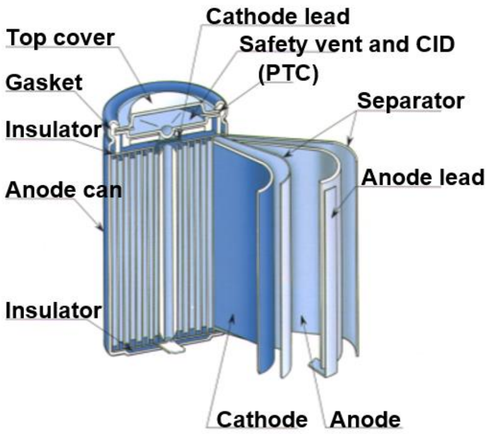
CHARTER: Develop battery technology that will enable large market penetration of electric drive vehicles

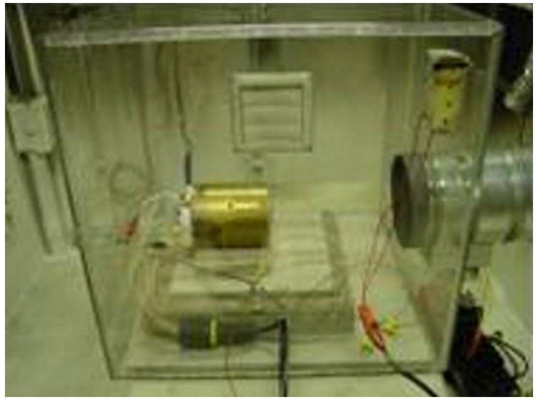
Cost Goal: $100/kWh$_{(useable)}$

Energy Storage R&D

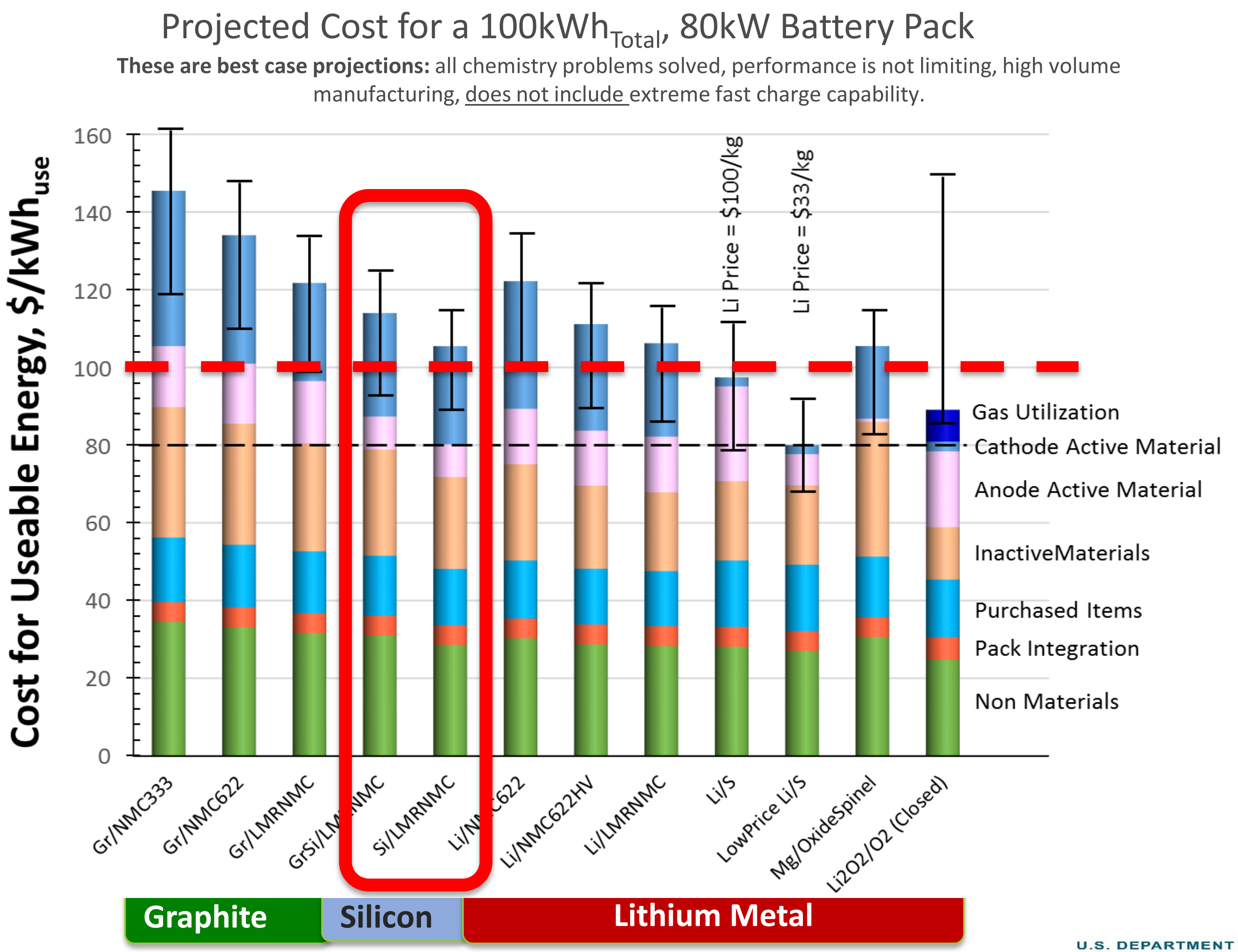
- **Battery Materials Research (BMR)**
- **Applied Battery Research (ABR)**
- **Battery Development**
- **Battery Testing, Design, & Analysis**







What Chemistries Can Help Meet DOE's Cost Goal?



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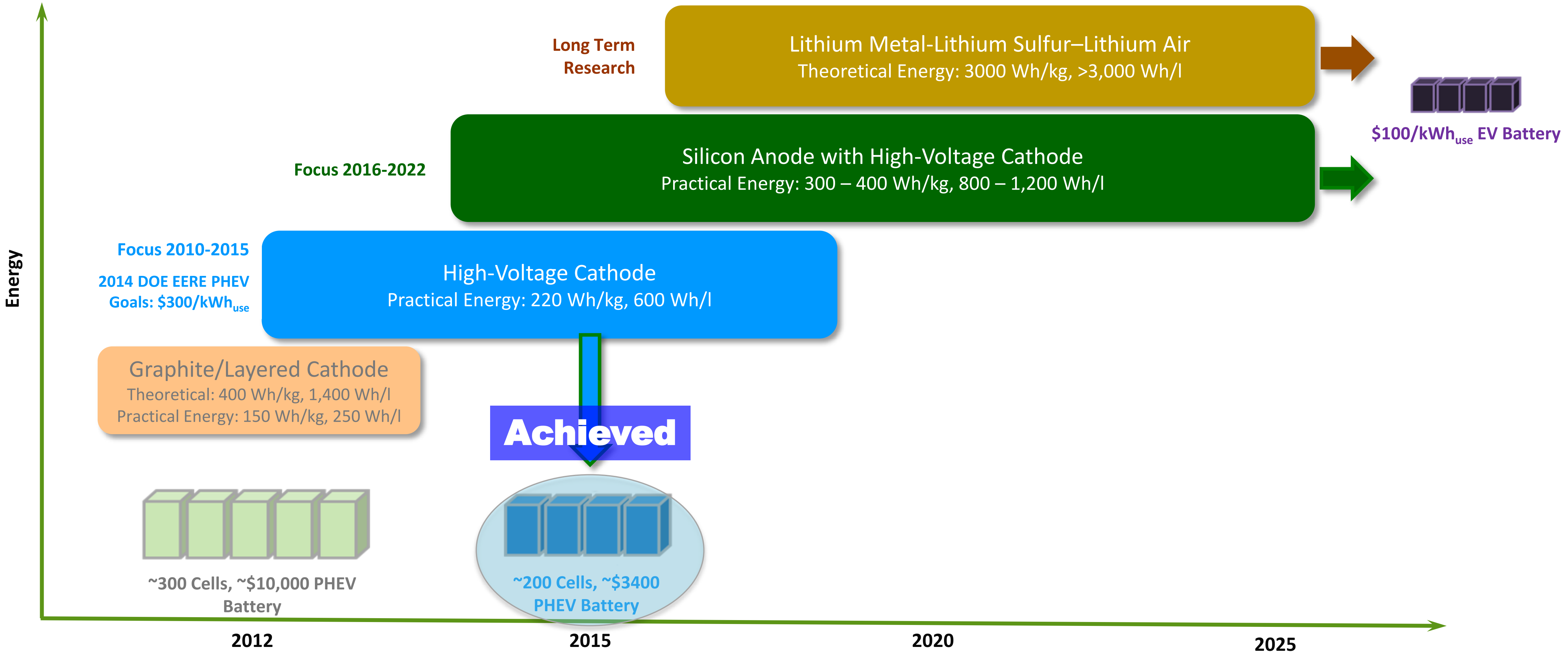
VTO R&D Materials Roadmap

Current emphasis: The development of high voltage cathodes and electrolytes coupled with high capacity metal alloy anodes. Research to enable lithium metal-Li sulfur systems.



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Silicon Anodes: Key Technical Results

Targets

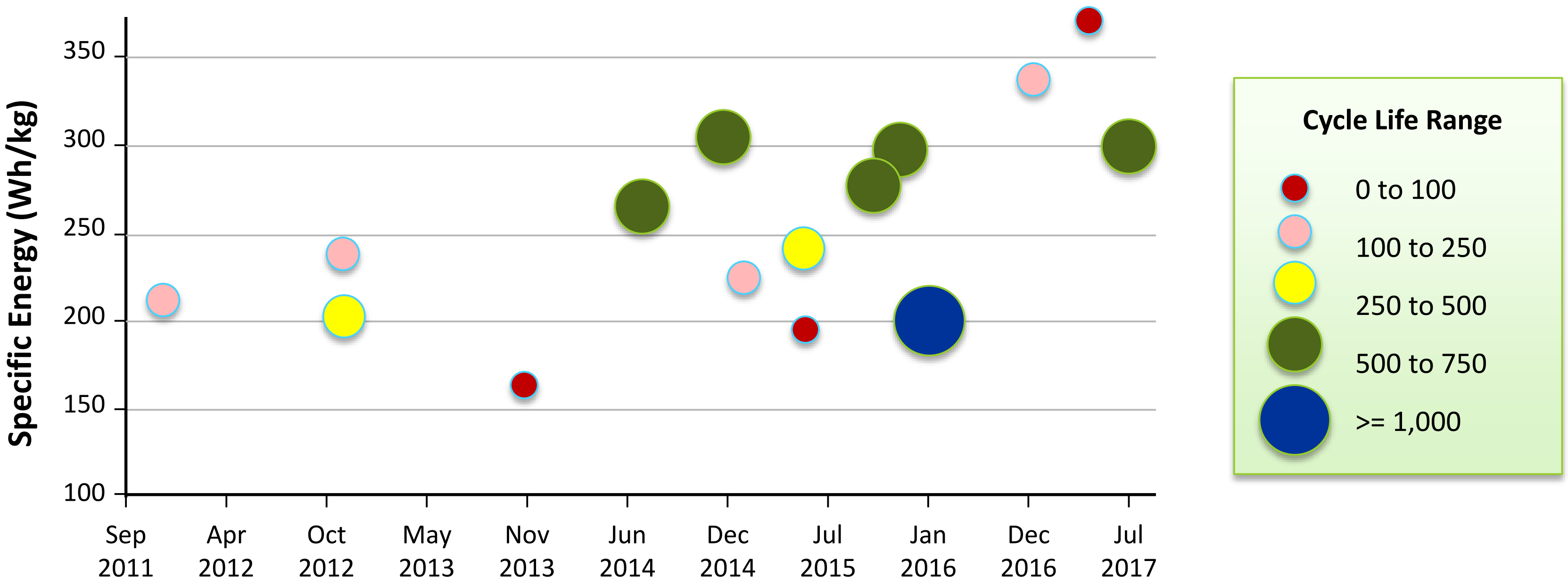
- 1,000+ mAh/g
- 10 years & 1000 cycles

Challenges

- Large first-cycle irreversible loss
- Low cycle and calendar life / High capacity fade

Specific Energy vs. Time

(Deliverables from DOE-funded Developers, data point size and color reflect cycle life)



VTO Energy Storage R&D Overview and Strategy for Silicon and Intermetallics

CHARTER: Develop battery technology that will enable large market penetration of electric drive vehicles

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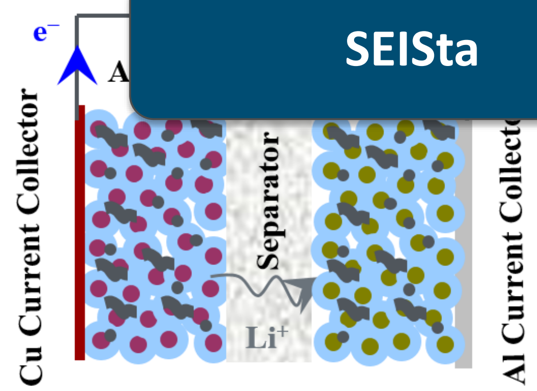
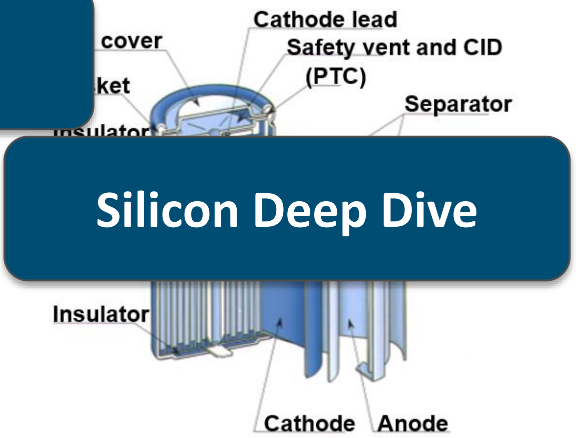
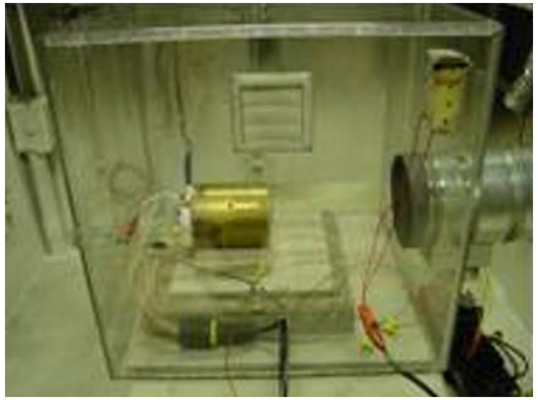
Energy Storage R&D

- **Battery Materials Research (BMR)**
  - SEISta
- **Applied Battery Research (ABR)**
  - Silicon Deep Dive
- **Battery Development**
  - USABC
  - FOAs
- **Battery Testing, Design, & Analysis**







Silicon Electrolyte Interface Stabilization Focus Group

Anthony Burrell

National Renewable Energy Laboratory

6/20/2018

Project ID # **ES333**

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

SEISta – Approach and Overview

<u>Overarching Mission:</u> Develop a stable SEI layer for Silicon Anodes to enable the use of intermetallic anodes for lithium ion batteries.

This is not a new challenge but we believe that the difficulties working with silicon have precluded a "quick fix" to long term stability of silicon electrodes.

We require a more foundational understanding of the formation and evolution of the SEI on silicon.

Understand first, fix later!

Approach

Critical Questions:

- What are the properties of the lithiated silicon electrolyte interface?
- What is the Silicon SEI actually made of and what reactions are contributing to it?
- How fast does the Silicon SEI grow?
- Does it stop growing?
- Is it soluble?
- Can it be stabilized?

Team work

- Coordination with the Deep Dive
- Understanding is critical
- Multiple characterization tools on the same problem
- Well characterized samples
- Standardized protocols
- Reproducibility across the team (multiple labs)
- Communication !!!!
  - All information is stored on BOX
  - Weekly team meetings (video)
  - Quarterly face to face
  - Multiple side phone meetings
  - Site visits by researchers to other labs

Face to Face meeting Jan 2018

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · BERKELEY LAB · OAK RIDGE National Laboratory · Argonne NATIONAL LABORATORY

Milestones FY18

Quarter 1 Milestone:

Have completed the selection and characterization (XPS, SIMS, IR, and Raman), including determination of the surface termination chemistry and impurity levels, of the SEISta model research samples to be used by all members of the team in FY18. 100% complete

Quarter 2 Milestone:

Have characterized (XPS, SIMS, IR, and Raman) the surface chemistry and composition of the SEISta model research samples after contact with the electrolyte, before cycling, including the nature of the electrolyte decomposition products. 100% complete

Quarter 3 Milestone:

Completed characterization (electrochemistry, IR and Raman) of the early stage silicon electrolyte interphase formation on the SEISta model research samples, specifically by establishing and demonstrating a procedure for quantitatively measuring the solubility of SEI on silicon surfaces.

Quarter 4 Milestones:

Established and demonstrated a procedure for measuring the growth rate of silicon SEI components at fixed potentials and during cycling.

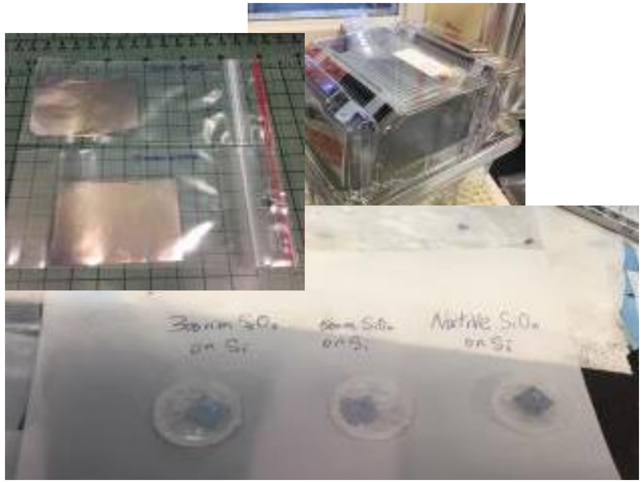
Have determined how the physical properties of the silicon electrolyte interface are influenced by the nature of the silicon surface on the SEISta model samples.

Development of Standard Handling Protocols, Test Procedures, Samples and Platforms is Critical to Success

Established protocols for sample synthesis, preparation, characterization and analysis to ensure compatibility of experimental data from all consortium members. complete.

Standard Procedures for everything

Standard materials supplied form single batches



Electrodes prepared and shipped form single source.

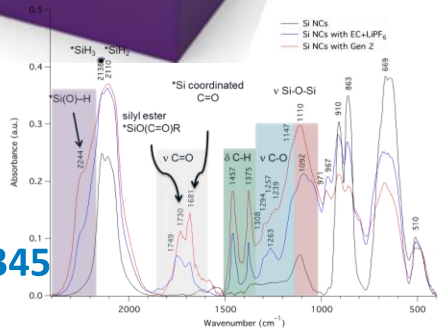
Baselines must be consistent across all partners. The life history of the silicon sample may play a critical role in the formation and evolution of the SEI. If each partner is not "making the same measurements on the same sample" then progress is going to be slow.

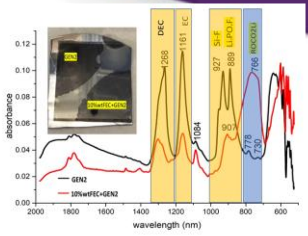
NREL Sandia National Laboratories Berkeley Lab Oak Ridge National Laboratory Argonne National Laboratory

Chemical reactivity vs electrochemical reactivity

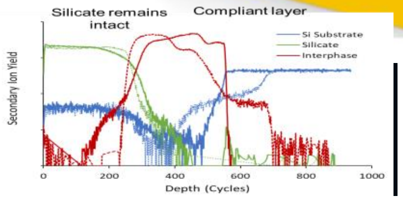
J. Phys. Chem. C 2017, 121, 14476−14483

Chemical Reactivity of Silicon Project ID BAT345



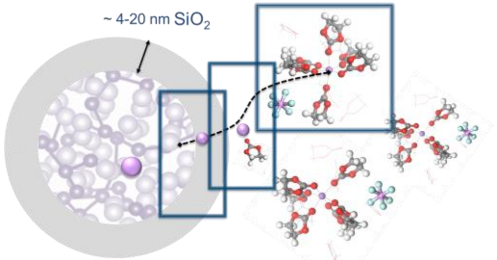


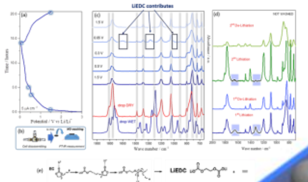
Surface analysis of the Silicon SEI ID BAT347

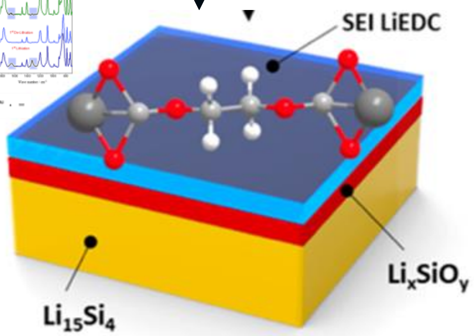


Role of Li Silicates in Si SEI Formation ID BAT348

Spectroelectrochemistry on silicon ID BAT364

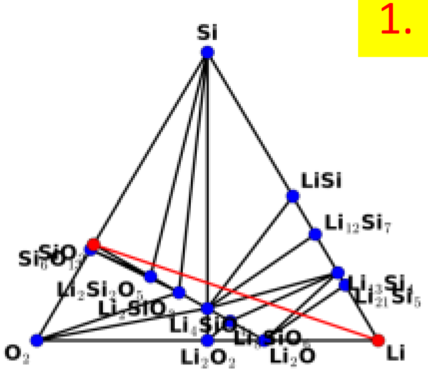






Predicting and Understanding Novel Electrode Materials From First-Principles Project ID BAT344

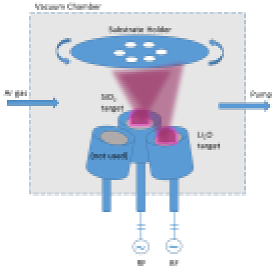
Thrusts for remainder of FY18: Lithium Silicate

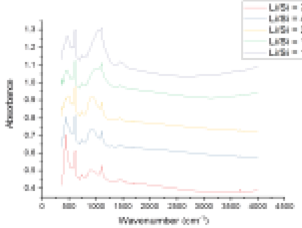


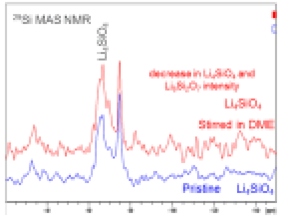
1. Understand the materials phase space

"Equilibrium" pathway for lithiation of crystalline SiO2 can be followed along the red line shown in the bulk Li-Si-O phase diagram obtained from the Materials Project database.

2. Prepare model compounds and surfaces

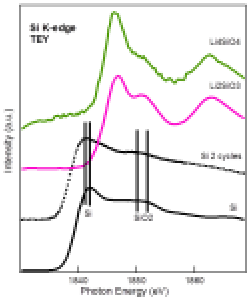


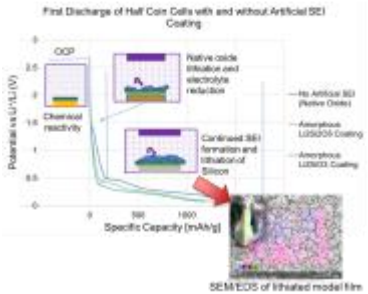




Using model lithium silicate thin film layers on silicon thin film anodes to determine effect of lithium silicate formation on evolution of silicon SEI

3. Understand the electrochemical evolution of the LixSiOy



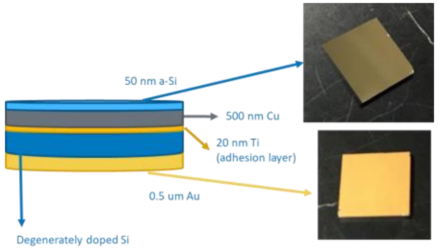


Do Lithium silicate films have an effect on the lithiation kinetics and SEI formation and evolution?

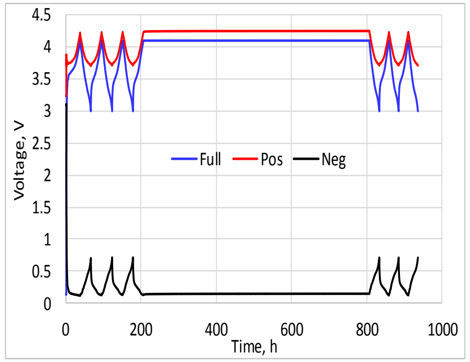
Thrusts for remainder of FY18: SEI Stability

We will focus a significant experimental effort to understand the different mechanisms that are present:

Careful electrochemistry on model electrodes



Precision electrochemistry coupled with detailed spectroscopy



Cycle Number	Charge Capacity mAh/g	Discharge Capacity mAh/g	Capacity Loss of Cycle mAh/g
1	178.5	138.4	40.1
2	139.8	135.1	4.7
3	136.3	133.4	2.9
4	133.7	129.3	4.5
5	125.6	124.8	0.8
6	124.6	123.7	0.9

The capacity of silicon containing cells show significant loss even in calendar studies. The expansion contraction of the silicon is not the only failure mechanism.

Does the SEI continue to grow? Does it dissolve? Are the specific parasitic reactions that limit stability!

The principle for selecting the samples is to decouple lithiation current versus corrosion/ passivation current. All Si electrodes must yield reproducible results under the same testing conditions. Therefore consistency of the key physico-chemical parameters of Si electrodes such as thickness, crystallinity, Si surface orientation is essential for the success of this research thrust.

Conclusions

- The nature and life history of the silicon has a dramatic effect on the formation and evolution of the SEI on silicon.
- Understanding the SEI on silicon will require multiple characterization techniques but if the samples and experiments are not "the same" then confusing results are obtained.
- A team approach with rigorous sample and experimental control is at the heart of this project.
- Understanding is the key to enabling silicon anodes and clear experimental data that is universally applicable is the goal

CONTRIBUTORS AND ACKNOWLEDGMENT

Alison Dunlop	Dennis Dees	Jinghua Guo	Robert Kostecki
Al-Jassim, Mowafak	Eric Allcorn	John Moseley	Robert Tenent
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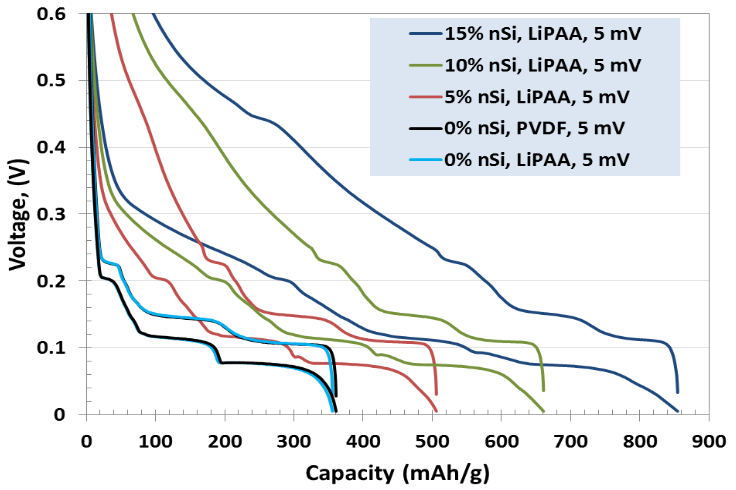
Anthony Burrell	Gao Liu	Kevin Zavadil	Stephen Trask
Atetegeb Haregewoin	Glenn Teeter	Kristin Persson	Steve Harvey
Aude Hubaud	Gregory Krumdick	Krzysztof Pupek	Taeho Yoon
Baris Key	Harvey Guthrey	Kyle Fenton	Tingzheng Hou
Brian Cunningham	Ira Bloom	Liang Zhang	Tomonori Saito
Bryant Polzin	Ivana Hasa	Linghong Zhang	Trevor Dzwiniel
Cameron Peebles	Jack Deppe	Lu Zhang	Vincenzo LaSalvia
Christopher Apblett	Jack Vaughey	Lydia Terborg	Wei Tong
Christopher Johnson	Jaclyn Coyle	Matthew Page	Wenquan Lu
Christopher Orendorff	Jagjit Nanda	Min Ling	William Nemeth
Chun Sheng Jiang	James Ciszewski	Nathan Neale	Yangping Sheng
Chunmei Ban	James Gilbert	Niya Sa	Yun Xu
Claus Daniel	Javier Bareno	Pauls Stradins	Zhengcheng Zhang
Daniel Abraham	Jianlin Li	Peter Faguy	Zhijia Du
David Wood	Jing Xu	Phil Ross	

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham, Steven Boyd, and David Howell

NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: OVERVIEW

Silicon Deep Dive



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VEHICLE TECHNOLOGIES OFFICE
2018 ANNUAL MERIT REVIEW

Next Generation Anodes for Lithium-Ion Batteries: Silicon Deep Dive Overview

- **Objectives: Stabilize the SEI - Stabilize the electrode**
- **Overall focus on insights into and advancement of silicon-based materials, electrodes, and cells.**
- **Advancements verified on life and performance of full cells using standardized testing protocols.**

- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP); Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study silicon composites and alternative high-energy metals.

Strong Interactions Between Silicon Anode Consortium Projects

Electrochemistry

Silicon Deep Dive

Joint Weekly Meetings

Shared Researchers

Raman Studies

Interfacial Studies

Analytical Diagnostics

IR Studies

Interface Modification

NMR Studies

Strong Communications

Collaborative Efforts

XPS Studies

Cycling Protocols

Silicon Electrolyte Interface Stabilization (SEI-Sta)

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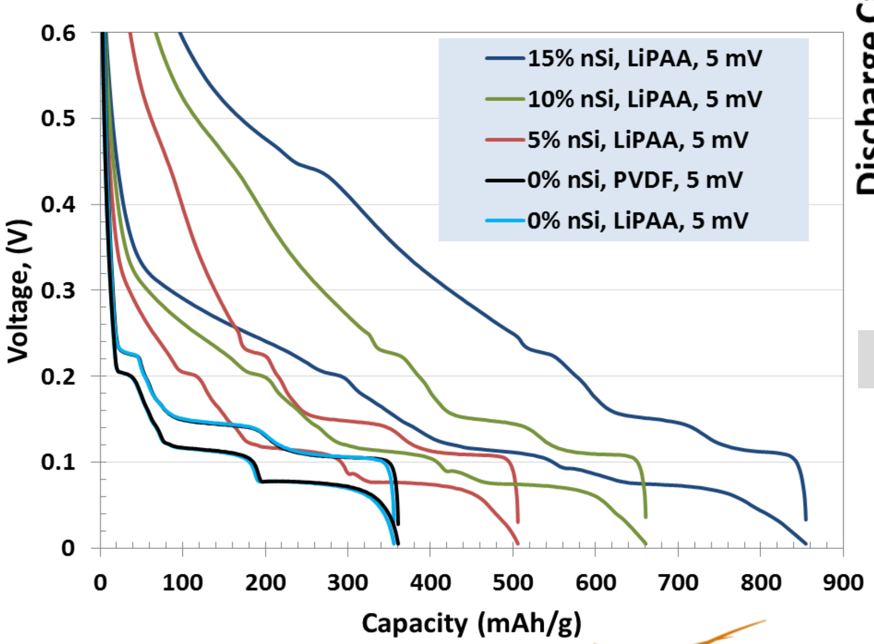
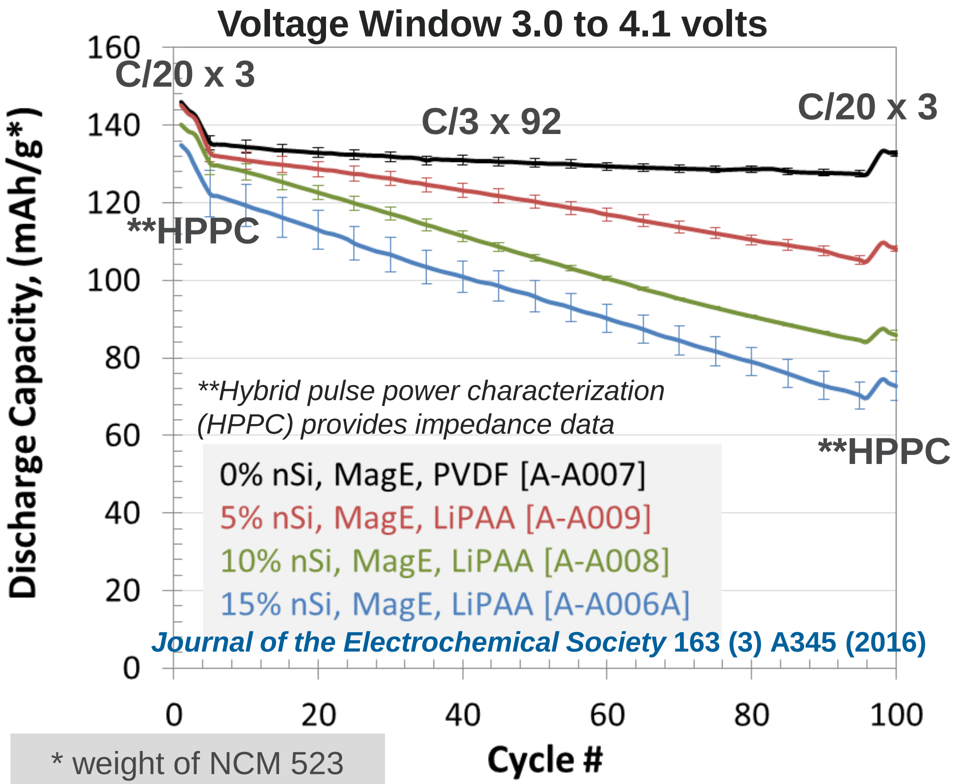
Advancements Verified on Life and Performance of Full Cells using Standardized Testing Protocols

As the Silicon content increases:
--- Energy increases
--- Increased voltage hysteresis
--- Lower current efficiency
--- Increased volume change

Half-Cells Voltage Profile



Full Initial Baseline Cells Capacity Fade



* weight of NCM 523

Anodes: A-A00_
92-73 wt% Hitachi MagE
0-15 wt% Nano&Amor Silicon (50-70nm)
2 wt% Timcal C45
10 wt% LiPAA (LiOH titrate)

Cathode: A-C013A
90 wt% Toda NCM 523
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

~2 mAh/cm^2 Electrodes
Matched to ~1.10 to 1.30 n:p ratio

Focus on Insights and Advancement of Silicon-Based Materials, Electrodes, and Cells

Highly integrated program based at six National Laboratories, presented in five technical presentations.

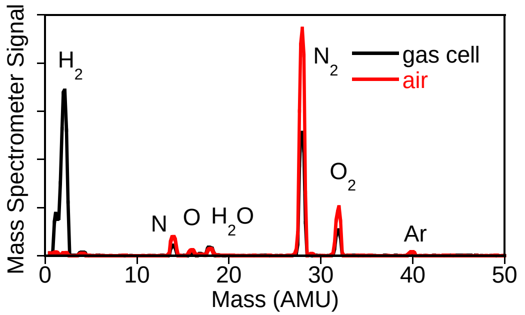
- BAT349: Research Facilities Support
  - Kyle Fenton
- BAT350: Electrode Characterization and Analysis
  - Steven Trask
- BAT351: Active Particle Studies
  - Baris Key
- BAT352: Active Materials Advancements
  - Zhengcheng (John) Zhang
- BAT353: Crucial Supporting Materials Advancements
  - Gao Liu

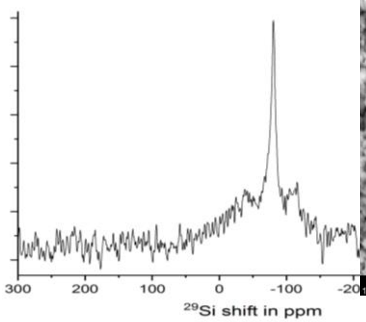
Industrial participation and/or collaboration that does not limit program innovation or the free flow of information is encouraged (e.g. Paraclete Energy is present baseline silicon supplier).

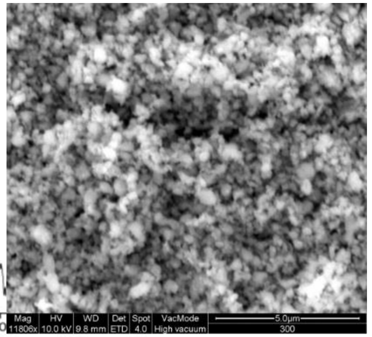
Strength of Silicon Deep Dive Effort is Based on Strong Researcher Interactions

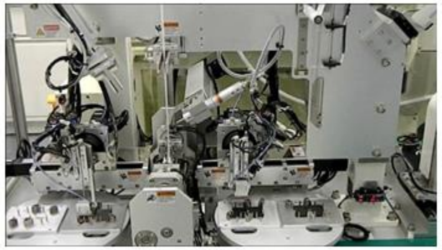
A few examples :

- BMF examines gassing and other issues during processing of silicon containing electrodes and works with the diagnostics effort to correlate to performance.
- NMR researchers conduct a number of fundamental studies, as well as, supporting the diagnostics effort and materials and process development.
- Post-Test facility conducts a broad range of diagnostics on aged cells and, in addition, its capabilities are used to characterize pristine and aged Si-based electrode materials and Li-Si phases.
- CAMP, with support from team, identifies and obtains baseline materials, fabricates electrodes and cells, and distributes across the complex.









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CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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- Baris Key
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- Robert Kostecki
- Gregory Krumdick
- Jianlin Li
- Xiaolin Li
- Min Ling
- Gao Liu
- Wenquan Lu
- Maria Jose Piernas Muñoz
- Jagjit Nanda
- Kaigi Nie
- Ganesan Nagasubramanian
- Christopher Orendorff
- Bryant Polzin
- Krzysztof Pupek
- Marco-Tulio F. Rodrigues
- Philip Ross
- Rose Ruther
- Niya Sa
- Robert Sacci
- Tomonori Saito
- Yangping Sheng
- Youngho Shin
- Ilya A. Shkrob
- Seoung-Bum Son
- Caleb Stetson
- Robert Tenent
- Lydia Terborg
- Wei Tong
- Stephen Trask
- Jack Vaughey
- Gabriel Veith
- David Wood
- Yimin Wu
- Koffi Pierre Claver Yao
- Taeho Yoon
- Ji-Guang Zhang
- Liang Zhang
- Linghong Zhang
- Lu Zhang
- Zhengcheng Zhang
- Tianyue Zheng

Support for this work from Battery R&D, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham, Steven Boyd, and David Howell

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